TOWARDS THE DEVELOPMENT OF FLEXIBLE CIGS SOLAR CELLS ON POLYMER FILMS WITH EFFICIENCY EXCEEDING 15%

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ABSTRACT

Development of $Cu(In,Ga)Se_2$ (called CIGS) solar cells on polymers is challenging because of the thermo-physical properties of layers and substrates. CIGS layers of suitable structural and opto-electronic properties should be grown at low temperature (< 500°C) as polyimides tend to degrade at higher deposition temperatures. Additionally, a method for controlled incorporation of an optimum amount of Na in CIGS is needed for high-efficiency cells since polyimides do not contain Na. Solar cells were developed on commercially available Upilex foils. CIGS layers were grown by evaporation of elemental Cu, In, Ga and Se at different substrate temperatures. Na from a NaF film was incorporated into CIGS layers with a post-deposition diffusion method that is suitable for in-line production of solar cells. Independent measurements have confirmed 14.1% efficiency under simulated AM1.5 standard test conditions. This is the highest efficiency reported to date for any kind of solar cell grown on polymer films. An average reflectance loss of about 13% was measured for these cells. Application of a commonly used anti-reflection coating would enable more than 15% efficiency flexible CIGS solar cells on polyimide foils.

I. INTRODUCTION

Thin-film solar cells based on $Cu(In,Ga)Se_2$ (CIGS) absorber layers on flexible substrates have a lot of advantages compared to CIGS cells prepared on (rigid) soda-lime glass (SLG): They are lightweight, they can be applied on uneven surfaces and they can be rolled up when not in use. So flexible CIGS modules open new applications possibilities for terrestrial use. Their excellent radiation tolerance and their high ratio of delivered power to module weight also make them ideal candidates for space use. From the industrial point of view, flexible cells offer the considerable advantage to allow manufacturing with a roll-to-roll deposition process, which would reduces production costs significantly.

Typical substrates for the processing of flexible cells are metal or polyimide foils. On stainless steel substrates, conversion efficiencies up to 17.5 % have been reported [1], while with Ti substrates, efficiencies up to 16.2 % were achieved so far [2]. Deposition on metallic substrates allows CIGS growth at substrate temperatures in the range of 520-600 °C, similar to cells on standard SLG substrates. Nevertheless, also low-temperature CIGS growth processes may be interesting for them, since the demands on diffusion barriers and insulation layers are less stringent [3].

Polymer substrates offer advantages for monolithically interconnected module development and for providing high specific power (kW/kg). However the thermal stability of polyimide (PI) films is limited, therefore solar cells on PI substrates have to be processed at substrate temperatures below 500 °C. Low-temperature CIGS growth processes to date resulted in efficiencies below 15 % on any substrate [4]. The highest reported conversion efficiencies achieved with CIGS cells on commercial PI foils are 13.2 % (without anti-reflection coating) [5] and 12.1 % (with anti-reflection coating) [6], while 12.8 % (without anti-reflection coating) were achieved on a non-commercial PI film [7].

The fact that neither metal nor polymer foils contain Na requires additional Na incorporation, since a small amount of Na (typically of the order of 0.1 at%) in the polycrystalline CIGS absorber layers is well known to increase cell efficiencies significantly. On SLG, Na would diffuse from the substrate through the Mo back contact during CIGS growth, but metal and PI foils need alternative Na incorporation methods to obtain highest cell efficiencies. The common alternatives are deposition of a Na-containing precursor layer (e.g. NaF, Na_2S, or Na_2Se) onto the Mo back contact prior to CIGS growth or co-evaporation of a Na compound during CIGS growth. In previous work, we have shown that also in-diffusion of Na into as-grown, Na-free CIGS layers leads to an improvement in cell performance [8]. In this paper we describe the development of flexible CIGS solar cells on polymer foils with the highest efficiencies reported to date.

II. EXPERIMENTAL DETAILS

We have grown CIGS solar cells on different commercially available polyimide (PI) foils. We found that for our processes Upilex-S (trade mark name) is better suited; different thicknesses were evaluated but most of the work was done on 12.5 μm thick Upilex-S foils. The

samples were carefully cleaned in isopropanol-aceton ultrasonic bath and finally rinsed with de-ionised water to remove electrostatic charges. Solar cells were grown on 5 x 5 cm^2 foils. For better handling during different deposition processes the Upilex foils were mounted between two specially designed frames. An approximately 1 μm-thick Mo back contact was directly deposited by dc sputtering without application of any additional intermediate layer. CIGS absorber layers were grown by evaporation of elemental Cu, In, Ga and Se and using the "3-stage" process [9]. During the 1st stage of absorber growth substrate temperature was kept at 400 °C, while during 2nd and 3rd stages the substrate temperature (in the following called $T_{sub,max}$) was kept at 400 °C or increased to <500 °C. Na in CIGS was incorporated in-situ by a post-deposition treatment (PDT) method. This consists of evaporation of about 30 nm NaF on CIGS, without substrate heating, and then annealing the sample at 400 °C for 20 minutes. Details of the CIGS deposition process and PDT method have been described elsewhere [10].

The solar cells were finished by deposition of a CdS buffer layer by chemical bath deposition, rf sputtering of i-ZnO/ZnO:Al front contacts (300 nm thick) and electron beam evaporation of Ni-Al contact grids for better current collection. No anti-reflection (AR) coating was applied. Current density - voltage (J–V) characteristics of solar cells were measured under simulated AM1.5 conditions at room temperature.

III. RESULTS AND DISCUSSION

First experiments were performed to ensure the improvements in cell efficiencies on PI films with PDT method. The results have shown that the in-diffusion of Na significantly improves the efficiencies. Typical consequence of the presence of Na during CIGS growth on the cell parameters, as reported in the literature [11-13] are substantial improvements in V_{OC} and FF, but hardly in J_{SC}. Since PDT Na incorporation gives rise to corresponding changes in the cell parameters, it is likely that the dominating Na mechanisms responsible for the
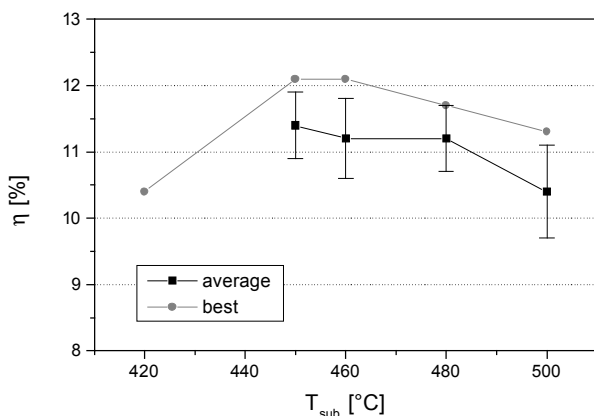
Figure 1: Cell efficiency vs. T_{sub}. Best cells are obtained at deposition temperature of 450-460 °C.

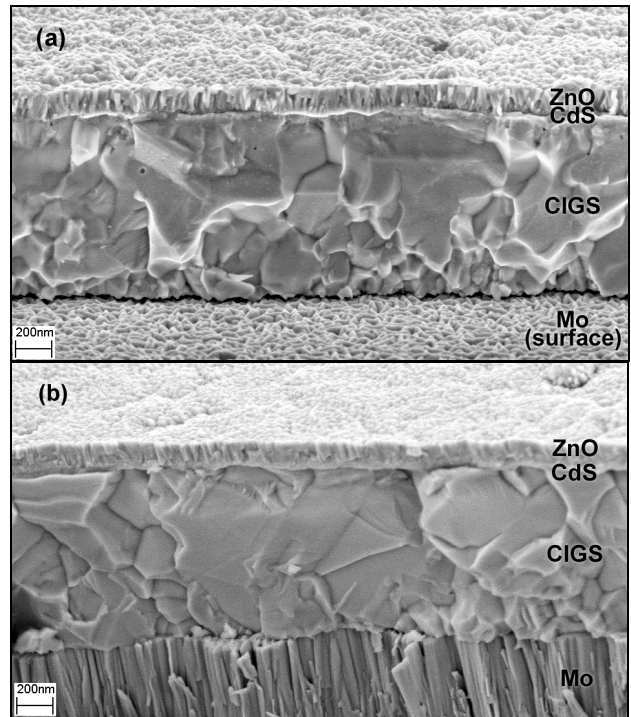**Figure 2:** Scanning electron microscope images of CIGS solar cells grown on polyimide substrates at $T_{sub,max}$ = 450 °C (a) and $T_{sub,max}$ = 500 °C (b) showing the cross-sections of the CIGS absorber, the CdS buffer, and the i-ZnO/ZnO:Al window layers. Grain sizes appear slightly larger at higher temperature.

improvements are the same, although CIGS growth kinetics, grain size and crystallographic orientation are not affected with PDT Na incorporation.

The presence of Na during CIGS growth leads to structurally and electronically modified absorber material, resulting for example in different grain sizes, smoother surfaces and increased net carrier concentration. The wealth of effects attributed to sodium has led to numerous suggestions of mechanisms that may be responsible for Na-induced cell efficiency improvements. However, although the importance of Na was realized more than a decade ago [14], no mechanism for the action of Na is commonly accepted. Experiments suggest that interaction of Na with grain boundaries in CIGS is the dominant mechanism responsible for improvements in layer and cell properties [15].

Absorber depositions at different $T_{sub,max}$ have shown that best efficiencies are obtained at $T_{sub,max}$ = 450-460 °C (Fig. 1). At higher temperature the efficiency of PDT processed cells are lower as also reported for cells grown on Al$_2$O$_3$ coated soda-lime glass (SLG) [15].

The cross-section scanning electron microscope (SEM) images of solar cells with CIGS absorbers grown at $T_{sub,max}$ = 450 °C (Fig. 2a) and 500 °C (Fig. 2b) show small grains of CIGS near the Mo back contact, but larger grains of dimensions approaching 1 μm are observed in the upper half of the CIGS layers. SEM images were
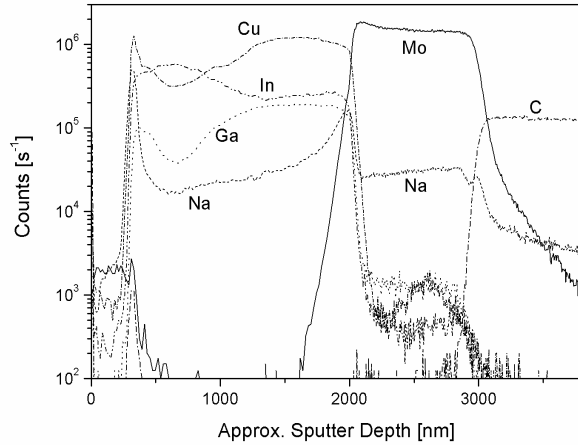
Figure 3: SIMS depth profile of CIGS/Mo layers in solar cells on PI. No C diffusion into absorber is detected. The Ga-dip/In-hill is due to low In-Ga interdiffusion at low temperature. The Cu-dip is a matrix effect and not real.

taken at a certain angle, therefore the layer thicknesses appear smaller than they really are. The actual thickness of the absorber layer is 1.7 μm and the ZnO-layer is 300 nm.

The structural difference between the two samples (Fig. 2) is small; the one grown at $T_{sub,max}$ = 500 °C seems to have slightly larger grains. Although solar cell component layers and substrate have different thermal expansion coefficients (Upilex: 12-24·10^{-6} K^{-1}, Mo: 4.8-5.9·10^{-6} K^{-1}, CIGS: 7.9-11.4·10^{-6} K^{-1}) [4], no cracks have appeared on the samples, even after high temperature deposition and/or after CBD-CdS and ZnO/ZnO:Al depositions. This required optimisation of Mo sputtering and CIGS deposition processes.

Secondary ion mass spectrometry (SIMS) measurements (Fig. 3) performed at Stuttgart University do not show carbon contamination from the substrate into the absorber layer, which suggests that no intermediate diffusion barrier is needed between the PI-substrate and Mo back contact. Na diffuses, as expected, through the whole absorber layer and can be observed even in the Mo layer and in the polyimide. Due to the low interdiffusion of Ga and In at low substrate temperature a Ga dip and In peak in composition profiles appear near the absorber surface, this results in a band-gap grading in the absorber layer. It should be clarified that the Cu dip is a matrix effect as cross-checked with several samples of different types. The band-gap grading (or composition profiles) depends on CIGS deposition temperature and the results are consistent with previous results on SLG [15].

Our CIGS deposition process was optimised for efficiency improvement. Figure 4 shows the current-voltage characteristics of a 14.1%-efficiency cell on PI (V_{oc} = 649.4 mV, FF = 69.1 %, J_{sc} = 31.48 mA/cm², total area = 0.595 cm²; no AR coating) measured under AM1.5 standard test conditions at the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany. This is the highest reported efficiency for any solar cell grown on a

polymer substrate to date.

As already mentioned, no AR coating was applied to the solar cells. Therefore the external quantum efficiency (EQE) does not exceed 80-85 % (Fig. 5). The low EQE between 400 nm and 550 nm wavelength comes from the photon absorption loss in the CdS buffer layer. Absorption at wavelength until 1200 nm confirms the presence of a band-gap grading of Ga and grains with low Ga content. The oscillation of EQE, most pronounced around 1000 nm, comes from the interferences in the reflectance. An average reflectance loss of about 13 % was measured in the visible-near IR spectral region for these solar cells. Therefore application of a commonly used anti-reflection coating would minimize the reflection loss to 2-4% [16] and a further gain of about 10% (relative) in efficiency would enable more than 15 % efficiency flexible CIGS solar cells on polyimide films.

IV. CONCLUSIONS

We have applied a low temperature (450 °C) CIGS deposition process and a reliable method for controlled incorporation of Na into CIGS with a PDT method to develop high-efficiency flexible CIGS solar cells on commercially available polyimide films. Independent measurements at Fraunhofer ISE Freiburg, Germany have confirmed an efficiency of 14.1 % without anti-reflection coating. Measurements of quantum efficiency and reflection loss suggest that application of a commonly used anti-reflection coating would enable more than 15 %-efficiency flexible CIGS solar cells on polyimide films. This process can also be used for high-efficiency cells on metal foils, since low deposition temperature will be effective in reducing metal impurity diffusion in CIGS, especially from stainless steel foils.
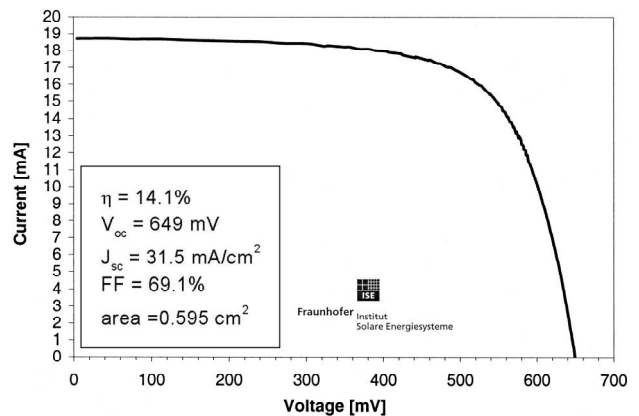

Figure 4: Current–voltage characteristics of a CIGS solar cell on a polyimide foil under AM1.5 standard test conditions. The efficiency of 14.1 % presents a world record for solar cells on polymer substrates. The measurement was certified by the Fraunhofer Institute for Solar Energy Systems in Freiburg, Germany. Na in the CIGS absorber layer was incorporated with a post-deposition treatment.
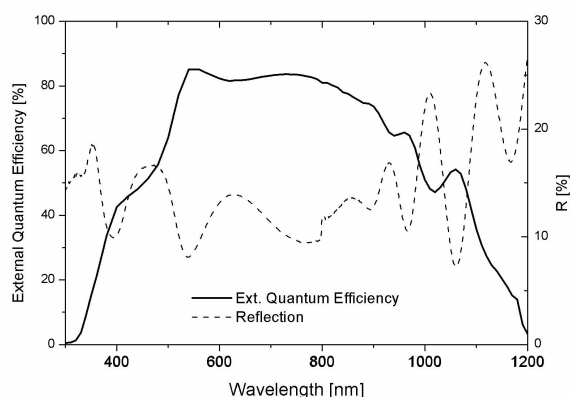
Figure 5: External quantum efficiency characteristics of a CIGS solar cell on a polyimide and the corresponding reflection from front contact (ZnO:Al) surface. An average reflectance loss of about 13 % was measured in the visible-near IR spectral region.

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